

California Environmental Protection Agency



**Air Resources Board**

Engineering and Monitoring Branch  
Monitoring and Laboratory Division

SOP MLD 022

**STANDARD OPERATING PROCEDURE FOR THE  
DETERMINATION OF CARBONYL COMPOUNDS  
IN AMBIENT AIR**

EFFECTIVE DATE: January 1, 1996  
APPROVAL DATE: October 5, 1998  
REVISION NUMBER: 4.0

DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedure are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

**State of California  
Air Resources Board  
Monitoring & Laboratory Division**

**S.O.P. MLD 022**

**Standard Operating Procedure for the Determination  
of Carbonyl Compounds  
in Ambient Air**

## **1 Scope**

This is a high performance liquid chromatographic (HPLC) method for the determination of formaldehyde, acetaldehyde, and methyl ethyl ketone (MEK) in the ambient air utilizing solid adsorbent. The method was developed from EPA Method TO11. Revision #4 utilizes an ozone scrubber upstream from the Sep-Pak DNPH-silica cartridge. This silica cartridge is more efficient in collecting formaldehyde from the ambient air than the C-18 cartridge which was used in Revision #3. The silica cartridge also has a lower acetone contamination than the C-18 cartridges.

## **2 Summary of Method**

- 2.1 Ambient air is drawn through chromatographic grade Sep-Pak silica cartridges. The cartridges are coated with acidified 2,4-dinitrophenylhydrazine (DNPH). Sampling rate is dependent upon carbonyl concentration but is sampled at 0.7L per minute for a 24-hour period. During sampling, formaldehyde, acetaldehyde, and methyl ethyl ketone react with the DNPH to form derivatives which are called hydrazones.
- 2.2 The DNPH derivatives are eluted from the sampling cartridges using acetone-free acetonitrile (ACN) and are quantified using reverse-phase HPLC with ultraviolet absorption detection at 360 nm.

## **3 Interferences/Limitations**

- 3.1 Since this procedure is written for the sampling and analysis of formaldehyde, acetaldehyde, and methyl ethyl ketone, possible interferences may be caused by the coelution of other aldehydes and ketones.
- 3.2 When commercially pre-coated DNPH cartridges are used, 2% of each production lot must be analyzed for impurities prior to use.

## **4 Apparatus**

- 4.1 A Waters gradient HPLC system consisting of mobile phase reservoirs; high pressure pumps; an injection valve or automatic sampler; a Waters Nova-Pak C-18 column 3.9 mm x 15 cm; a variable wavelength UV detector operating at 360 nm; and a data system.
- 4.2 Sampling system - a XonTech Module 920 Multi-media sampler fitted with a sampling head configured to hold the Sep-Pak DNPH-silica cartridges and capable of sampling at a flow rate of between 0.5 and 2.0 LPM.
- 4.3 Supelco 4 mL glass desorption vials with Teflon lined screw caps. Sun brokers 1 mL autosampler "Sun Vial" with polyethylene cap septum.
- 4.4 Sample rack to hold cartridges during elution.
- 4.5 Filtration and degassing system for mobile phase solvents such as Waters Part #85124.
- 4.6 Various volumetric pipets and flasks and graduated cylinders.
- 4.7 Polyethylene gloves - used to handle the treated cartridges.
- 4.8 Whatman 3.7 cm, #41 ashless filter paper.

## **5 Reagents**

- 5.2 Acetone-Free Acetonitrile and water mobile phase solvents, HPLC grade such as Burdick & Jackson Product #016 and Baker #4218-3, respectively.
- 5.3 Sep-Pak DNPH-silica cartridges - Waters Chromatography.
- 5.4 Calibration Standards solutions or hydrazone crystals can be purchased from Radian Corporation or Supelco.
- 5.5 Potassium iodide --A.C.S. reagent grade .

## **6 Preparation of DNPH-Carbonyl Standards and Ozone Scrubber**

- 6.1 Standard Preparation
  - 6.1.1 Prepare a standard stock solution of the DNPH-carbonyl derivative by dissolving 10mg of hydrazone crystals in 100 mL of acetonitrile. Stock solutions are also available from Radian or Supelco.

6.1.2 Prepare a working calibration standard mix from the laboratory or vendor standard stock solution. The concentration of the DNPH-carbonyl compound in the standard mix solutions should be adjusted to reflect relative distribution in a real sample. The working standard concentrations should range from 0.05 to 2.0ug/mL as aldehyde or ketone.

6.1.3 Store all standard solutions in a refrigerator. They are stable for several months.

## 6.2 Ozone Scrubber Preparation

6.2.1 Prepare a 0.6M KI in deionized water. Dip the 3.7cm Whatman filter into the KI solution twice and let it dry. Upon drying, the filter should be placed between the two black rings and assembled.

## 7 Sampling

7.1 A XonTech Model 920 sampler is used to draw the ambient sample through the cartridges.

7.2 Remove the Sep-Pak cartridge and ozone scrubber from the transport containers. Place the cartridge and ozone scrubber in the appropriate holders and make sure that the holders are tightened properly.

7.3 Expose the Sep-Pak cartridge to 0.7 LPM ambient air for 24 hours. After the run, remove the Sep-Pak cartridge, recap it and put back in the transport container along with the 920 "printout" for the sampling period.

7.4 The aldehyde sampling is to be done on the same schedule as that for "Toxics" and therefore the transport container can be placed in the canister box for shipment back to the lab.

7.5 Upon receipt at the lab, the Sep-Pak should be placed in cold storage until elution.

## 8 Sample Analysis

### 8.1 Sample Desorption

8.1.1 Remove the Sep-Pak cartridges from the transport tube and connect each to a clean syringe.

8.1.2 Place the cartridge/syringe in the syringe rack and backflush the cartridge (gravity feed) with 5 mL of acetonitrile to a 5 mL volumetric flask.

8.1.3 Dilute to the 5 mL mark with ACN. Label the flask with sample ID.

## 8.2 HPLC Operating Parameters

### 8.2.1 The operating parameters are as follows:

Column: Nova-Pak C-18 (3.9mm x 150mm) operated @ room temperature.

<u>Gradient Program:</u>	Time (min)	%A	%B	%C
	0.0	100	0	0
	2.0	100	0	0
	13.0	25	75	0
	13.5	0	0	100
	14.5	0	0	100
	15.0	100	0	0
	21.0	100	0	0

where:

A = 60% Water : 30% Acetonitrile : 10% THF  
B = 60% Acetonitrile : 40% Water  
C = 100% Acetonitrile

Detector: Waters Model 490 UV/VIS at 360 nm. Sample rate 2 point/sec and 1.00 AUFS.

Flow Rate/Run Time/Injection Volume: 1.0 mL/min.; 33 minute run; 20 uL.

Retention Time:

Formaldehyde ~ 5.0 minutes  
Acetaldehyde ~ 7.3 minutes  
MEK ~ 16.0 minutes

8.2.2 Equilibrate the column for 30 minutes before first analysis. Analyze a blank to check for method interferences.

8.2.3 Calibrate the instrument using three standard concentrations each analyzed in triplicate. The results are used to prepare a calibration curve. Linear response is indicated when an r of at least 0.995 for a linear least squares fit of the data is obtained. The retention times for each analyte should agree within 5%.

- 8.2.4 Check the calibration of the instrument for each run by analyzing a control sample. The concentration given must fall within the UWL and LWL of the control sample value ( $\pm 2$  S.D.) Plot all results on the method control chart. The day to day response for the various standards should be within 10%.
- 8.2.5 Prepare a multimethod routine to control the automatic sampler. Run one injections per sample and a control standard for every ten samples.

## 9 Calculations

$$\mu\text{g}/\text{M}^3 = \frac{(\mu\text{g}/\text{mL})(\text{mL of extract})(1000)}{(\text{minutes sampled})(\text{LPM air flow})}$$

## 10 Method Sensitivity and Precision

<u>Formaldehyde conc. (<math>\mu\text{g}/5\text{mL}</math>)</u>	<u>0.10</u>	<u>0.25</u>	<u>2.50</u>	<u>5.00</u>	<u>10.00</u>	<u>20.00</u>
Peak Area	7241	21532	232486	469564	923725	1875779
Std. Deviation	661	1864	5436	18634	18096	49557
Coeff. Of Variation (%)	9.13	8.66	2.34	3.97	1.96	2.64

Correlation Coefficient: 0.9999  
 Slope: 93739.15  
 Intercept: -3113.36  
 MDL: 0.05 ug/5mL (|intercept|+ 3 (Std.Dev./Slope))

<u>Acetaldehyde conc. (<math>\mu\text{g}/5\text{mL}</math>)</u>	<u>0.10</u>	<u>0.25</u>	<u>2.50</u>	<u>5.00</u>	<u>10.00</u>	<u>20.00</u>
Peak Area	6083	13389	178885	363183	714580	1456390
Std. Deviation	557	2203	2700	12725	13483	38640
Coeff. Of Variation (%)	9.16	16.00	1.51	3.50	1.89	2.65

Correlation Coefficient: 0.9999  
 Slope: 72854.71  
 Intercept: -4454.23  
 MDL: 0.08 ug/5mL (|intercept|+ 3 (Std.Dev./Slope))

<u>MEK conc. (<math>\mu\text{g}/5\text{mL}</math>)</u>	<u>0.10</u>	<u>0.25</u>	<u>2.50</u>	<u>5.00</u>	<u>10.00</u>	<u>20.00</u>
Peak Area	3582	9560	108896	219386	429263	877589
Std. Deviation	734	1473	2147	8127	10679	23170
Coeff. Of Variation (%)	20.5	15.4	1.97	3.70	2.49	2.64
Correlation Coefficient:	0.9999					
Slope:	43843.01					
Intercept:	-2075.91					
MDL:	0.09 $\mu\text{g}/5\text{mL}$ ( $ \text{intercept}  + 3 (\text{Std.Dev.}/\text{Slope})$ )					

**NOTE:** MDL (Method Detection Limit) reported here is the instrument detection limit and therefore does not include any matrix factor.

To convert the unit of MDL in microgram per cubic meter air, the following equation is used.

$$\mu\text{g}/5\text{mL} = \mu\text{g}/\text{M}^3$$

(1  $\text{M}^3$  of air is sampled and concentrated in 5 mL of acetonitrile)